King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Preconcentration and simultaneous spectrophotometric determination of copper and mercury by dispersive liquid–liquid microextraction and orthogonal signal correction–partial least squares

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Abstract A new method for spectrophotometric simultaneous determination of copper and mercury was developed by the dispersive liquid–liquid microextraction (DLLME) preconcentration and orthogonal signal correction–partial least squares (OSC–PLS). In the proposed method, dithizone was used as a chelating agent, and carbon tetrachloride and acetonitrile were selected as extraction and dispersive solvents. All factors affecting the sensitivity were optimized by the Box–Behnken design and the linear dynamic range for determination of copper and mercury was found. Under the optimum conditions, the calibration graphs were linear in the range of 10.0–250.0 and 10–300 ng mL^{-1} with detection limit of 2.6 and 2.8 ng mL^{-1} ($3\delta_B$/m) and the enrichment factor of this method for copper and mercury, reached 180 and 175, respectively. The simultaneous determination of copper and mercury by using spectrophotometric methods is a difficult problem, due to the spectral interferences. The PLS modeling was used for the multivariate calibration of the spectrophotometric data. The OSC was used for preprocessing of data matrices and the prediction results of model, with and without using OSC, were statistically compared. The experimental calibration matrix was designed by measuring the absorbance over the range of 400–700 nm for 25 samples. The root mean squares error of prediction for copper and mercury with and without OSC was 0.010, 0.026 and 0.055, 0.086, respectively. The proposed method was successfully applied for the simultaneous determination of copper and mercury in spiked water and synthesis samples.

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1. Introduction

Nowadays the pollution of different natural waters by heavy metals is a great concern because of the toxic effects on living organisms. Urbanization, industrial development, and heavy traffic lead to contamination of water bodies by heavy metals.

Copper is a widespread anthropogenic pollutant of environment and the determination of this metal is the actual problem. However, high amounts of copper can be harmful, causing irritation of nose and throat, nausea, vomiting, and diarrhea. Mercury is one of the toxic heavy metals and as an introduced contaminant in the environment. The toxicity of mercury depends on its chemical species and it is found that organomercurials are more toxic than inorganic mercury compounds. Thus the development of new methods for separation, preconcentration and determination of these metal ions at trace levels in environmental is one of the targets of analytical chemists, due to their important roles in our life.

Several procedures have been developed for the separation and preconcentration of copper and mercury from environmental matrices such as: liquid–liquid extraction (Kara and Alkan, 2002), co-precipitation (Doner and Ege, 2005 and Zhang et al., 2004), solid phase extraction (Starvin and Prasada Rao, 2004; Tobiasz et al., 2012; Walas et al., 2008) and cloud point extraction (Gao et al., 2010; Niazi et al., 2009; Shoaee et al., 2012). However, liquid–liquid extraction (LLE) is time-consuming and requires large amounts of organic solvents that are potentially toxic. Solid phase extraction (SPE) uses much less solvent than LLE but can be relatively expensive. Additionally, evaporation of the final organic extract into a small volume is necessary to achieve high enrichment of the analytes. Batch-to-batch reproducibility continues to be the major concern for analysts in selecting SPE devices. Elution of sorbed solute must be performed after sample loading. Solvent evaporation and redissolution are often required (Nagaraju and Huang, 2007).

A novel microextraction technique as a high performance and powerful preconcentration method termed as dispersive liquid–liquid microextraction (DLLME) was demonstrated by Rezaee et al. (2006). In this method, an appropriate mixture of the extraction solvent and the dispersive solvent are injected into aqueous sample by a syringe and forms a cloudy solution. The cloudy state results from the formation of fine droplets of the extraction solvent which disperse in the sample solution. The cloudy solution shall be centrifuged and the fine droplets sediment at the bottom of the conical test tube. Determination of analytes in the remained phase can be performed by instrumental techniques. Recently, several papers have been published about the dispersive liquid–liquid microextraction in preconcentration and determination of metals (Bidari et al., 2007; Fan, 2007; Gharehbaghi et al., 2008; Liang and Sang, 2008; Liang et al., 2009; Naseri et al., 2008; Rivas et al., 2009; Xiao-Huan et al., 2009).

Spectrophotometric methods are the most commonly used techniques and continue to enjoy wide popularity. The common availability of the instrumentation, the simplicity of procedures, speed, precision, accuracy and low-operating costs of the technique still make spectrophotometric methods attractive. In the present work, the DLLME was combined with UV–Visible spectrophotometry by using micro-sample introduction system for the simultaneous determination of copper and mercury was proposed. In this method, dithizone, which forms complexes with copper and mercury, was selected as chelating reagent. Dithizone contains azo and hydrosulfide groups, which are good electron donors. Dithizone is widely used in extraction spectrophotometry because it can form stable complexes with many metal ions under proper conditions. The factors influencing the efficiency of DLLME and

determination of copper and mercury were systematically studied and optimized by the Box–Behnken design (Khajeh, 2009). Box–Behnken is a second-order multivariate design technique based on three-level incomplete factorial designs that received widespread application for evaluation of critical experimental conditions, that is, maximum or minimum of response functions (Macedo et al., 2009).

The simultaneous determination of several compounds in a mixture can be a difficult problem, especially for components that have similar analytical characteristics. The problem is how to distinguish overlapped signals that are often encountered in analytical experiments. Quantitative simultaneous spectrophotometry has been greatly improved by the use of multivariate statistical methods such as the PLS method. PLS modeling is a powerful multivariate statistical tool and can be performed with easily accessible statistical software (Brereton, 2000; Geladi and Kowalski, 1986). The basic concept of PLS was originally described by Gerlach et al. (1979) and Joreskog and Wold (1982), and consequently different applications for PLS modeling were reported (Ni et al., 2008; Niazi et al., 2005, 2007; Zapata-Urzua et al., 2010). Wold et al. (1988) introduced OSC as a pre-processing step that improves the calibration model by filtering strong structured (i.e. systematic) variation in X that is not correlated to Y. Therefore, one can be certain that important information regarding the analyte is retained. Since then, several groups (Andersson, 1999; Fearn, 2000; Pierna et al., 2001; Sjoblom et al., 1998; Westerhuis et al., 2001; Wold et al., 2001) have published various OSC algorithms in an attempt to reduce model complexity by removing orthogonal components from the signal. Recently, application of OSC in UV–Visible spectrophotometry simultaneous determination by PLS is reported (Khajehsharifi et al., 2009; Niazi et al., 2008; Niazi and Goodarzi, 2008; Niazi and Yazdanipour, 2007).

The aim of this study was to investigate, the possibility of using DLLME for simultaneous spectrophotometric determination of copper and mercury, in synthetic and real matrix samples such as different water samples, for the first time. The results obtained, with and without using OSC algorithm as a preprocessing treatment of original data, were compared. To our knowledge this is the first spectrophotometric report with DLLME extraction on the simultaneous determination of copper and mercury.

2. Experimental

2.1. Instrument and software

A Hewlett–Packard 8453 diode array spectrometer controlled by a Hewlett–Packard computer and equipped with a 100 μL quartz cell was used for recording the spectra. A centrifuge (Behdad Universal Centrifuge) was used to accelerate the phase separation process. The pH was determined with a model 780 Metrohm pH-meter with combined glass-calomel electrode.

PLS and OSC programs were written in MATLAB Version 6.5 (Math works Inc.). All programs were run on a personal computer (CPU 3.0 GHz and RAM 4 GB) with Windows XP operation system. Box–Behnken design was accomplished with Minitab Version 15. The OSC version applied here is based on the Wold algorithm (Wold et al., 1988).